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AMMONIA, METHANOL AND NITROGEN OXIDES

AIR EMISSION CONTROL

IN AMMONIA PLANTS

PREPARED BY

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SUMMARY

The Farmland Industries, Inc. developed process for the simultaneous control of the air emissions ammonia, methanol, and nitrogen oxides is presented herein. It combines a low pressure process condensate stripper with a non-condensables scrubber and recycle. The system is now in operation at two Farmland ammonia plants and is covered by two recently issued patents and four patents pending. A third unit is scheduled for start up in the Summer of 1996.

The use of Process Condensate Strippers (PCS) in the ammonia industry has been common practice for many years. Primarily, low pressure steam strippers operating at 5-20 psig (0.34-1.38 bar) are used with the contaminants vented to the atmosphere while reducing the concentration of ammonia, methanol and amines to sufficiently low levels that permit recovery and reuse of the condensate. This paper presents the Farmland Industries developed process for retrofitting an existing low pressure process condensate stripper for the recovery and recycle of ammonia, methanol, and amines for the primary purpose of eliminating these air emission contaminants. Concurrently, the system can include the removal of ammonia from low pressure purge gas thus reducing ammonia burned in the reformer that would otherwise elevate NO_x emissions from the reformer stack. The Farmland method utilizes existing or low cost readily available low pressure used equipment. The discussion includes the system operating and design conditions as well as the typical levels of emissions encountered and controlled.

DISCUSSION

The Clean Water Act and the need for high quality mineral free water resulted in the use of low pressure process condensate strippers in the ammonia industry many years ago. Process condensate from the ammonia plant raw gas separator (102-F in MWK plants) is contaminated with ammonia, methanol and traces of amines. The majority of the contaminants are formed as byproducts in the ammonia plant front end that are condensed and separated in the raw gas separator. Small quantities are also found in condensate from the CO₂ removal step in the regeneration of MEA or hot potassium carbonate and following cool down after methanation (condensate from 104-F in MWK plants).

In the preparation of synthesis gas, methanol is formed as a byproduct in the presence of the copper based low temperature shift catalyst where hydrogen and carbon monoxide react forming methanol (1). In another side reaction, the traces of ammonia formed in the upstream processing react with methanol to form methyl amine, dimethyl amine and trimethyl amine. Concentrations of ammonia and methanol in process condensate and amounts formed vary quite widely dependent on process variables such as steam-to-gas ratio, catalysts, catalyst condition and age, temperature, pressure, etc.

The amount of ammonia and methanol found to be formed then stripped and vented from process condensate strippers is stated in AP-42, air emission factors (2), to be 2.2 pounds of ammonia per ton (1.1 Kg/MT) of ammonia produced and 1.2 pounds of Volatile Organic Compounds (VOC) per ton (0.6 Kg/MT) of ammonia produced. The VOC is primarily methanol. Data from Farmland and other producers based on stack analysis and material balances on LP strippers give the following ranges:

Ammonia PCS Vent	1 .0-3.0 lb/ST NH, produced (0.5-1 .5 Kg/MT)
Methanol PCS Vent	0.5-2.0 lb/ST NH, produced (0.25-1 .0 Kg/MT)

The concentrations of ammonia and methanol in process condensates vary with the yield rate as discussed above as well as steam/gas ratio which influences the condensate recovery rate as does the raw gas separator temperature. Concentration ranges for these contaminants typically are:

Ammonia	400-2,000 PPM (wt) in Condensate
Methanol	200-1,000 PPM (wt) in Condensate

Little information is available on the concentration of methyl amines in process condensate however, it generally is believed that the concentration is less than 50 ppm.

The typical LP process condensate stripper flow scheme is illustrated in Figure 1 with the steam being vented to the atmosphere or in some cases vented to the reformer fire box converting a good deal of the NH₃ to NO_x, also not a good environmental situation. The most common LP PCS is a packed tower operating at 5-20 psig, using low pressure 50 psig (3.45 bar) supply steam at a rate of 1 .0-2.0 lb steam/gal (120-240 Kg/M³) of stripped water, with a liquid feed rate of 5.0-20.0 GPM/Ft² (0.2-0.8 M³/Min/M²) and a column vapor load parameter Fs of 0.5-2.0. Fs is a measurement of column load and is equal to the superficial vapor velocity in feet/second times the square root of the vapor density in pounds/cubic foot. The stripped condensate is usually taken down to 10 ppm NH₃, or less. Process design considerations are well established and presented in (3) and (4). The importance of consistent uniform liquid distribution is brought out in (5) and has been confirmed at Farmland.

Air emissions from LP process condensate strippers can be the largest single Toxic Release Inventory (TRI) emission source in an ammonia complex dependent on the plant and upgrading units at the site. Ammonia and methanol are among several hundred chemicals that must be reported as emissions to the U.S. Environmental Protection Agency annually on the TRI Form R. The combined emission rate for ammonia and methanol can easily exceed 1,000,000 lb/yr (454,000 Kg/Yr) in the case of a large ammonia plant. In the interest of controlling and eliminating this major TRI source, Farmland undertook the

development of a method that utilizes an existing LP carbon steel stripper without having to resort to the installation of a capital intensive high pressure stripper that operates at 400-600 + psig (27.6-41.4 bar). A typical high pressure steam stripper configuration is presented in Figure 2. The Farmland developed low pressure system is covered in U.S. Patents No. 5,385,646(6) and 5,498,317(7). In addition, four patents on the system are now pending.

The Farmland developed method of air emission control with a low pressure process condensate stripper is described in detail in (6) and (7) and appears in Figure 3. In essence, a conventional low pressure carbon steel stripper is converted by adding a rectification section, the purpose of which is to concentrate the contaminants to such a high level that a slip stream can be removed and injected into the ammonia plant with insignificant thermal impact. The slip stream can be injected ahead of the mixed feed coil or the air coil. There are a number of other possibilities as well.

As shown in Figure 3, a retrofitted tower has a rectification section added along with overhead condenser, overhead receiver/vent gas scrubber, reflux pump and injection pump. The small diameter vent scrubber is for the purpose of removal of final traces of methanol and ammonia from the noncondensables. This relatively low flow of gas is primarily carbon dioxide, hydrogen and nitrogen that entered in the stripper process condensate feed.

The Lawrence LP PCS was modified according to Figure 3 and started up in October 1994. In the Lawrence retrofitted unit, contaminants are concentrated around 100 fold over what they are in the 300 GPM (1.1 $4M^3$ per minute) stripper feed yielding a stream of about 3 GPM that is injected into the steam to the mixed feed coil. The thermal impact is insignificant in that steam superheat drops less than 10°F (5.6°C) and the temperature exit the mixed feed coil does not measurably change. The stripped process condensate typically has an ammonia level of 1 ppm. Reduction of the stripper emissions of ammonia, methanol and amines has been measured at better than 99%. The annual TRI reduction is over 1 ,000,000 lb/yr (454,000 Kg/Yr). The investment cost for the Lawrence Plant PCS retrofit was about \$500,000.

The second Farmland LP PCS system was started up in December 1995 at the Pollock, LA ammonia plant processing around 350 GPM (1.33 M^3 per minute) of condensate. Its configuration is shown in Figure 4. It differs from the Lawrence Plant in that it also processes low pressure purge gas from 107 F and 109 F (MWK Plant) through the vent gas scrubber to remove ammonia prior to venting the gas to the primary reformer. At an efficiency of better than 99%, the amount of ammonia removed is around 150 pounds (68 Kg) per hour. This results in substantially less reformer NO_x emission than would be released were

the ammonia to be burned in the reformer. When at near 1500 STPD (**1361** MTPD) ammonia plant rate the reformer stack was analyzed for NO_x with low pressure purge being directly (no ammonia removal) burned in the reformer. The analysis showed a NO_x concentration of 323 ppm expressed as NO_x. When the ammonia in the purge gas was removed (see Figure 4) before burning in the reformer, the analysis for NO_x was 95 ppm in the stack. The stack testing was performed by an outside emission testing firm.

The Pollock Plant stripped process condensate has analyzed C 1 PPM ammonia at a stripping steam rate of less than one pound per gallon of stripped condensate. The Pollock PCS utilizes direct injected steam whereas the Lawrence unit uses a reboiler which was in service prior to the retrofit. The Pollock PCS system was an all new installation at that plant requiring the equipment illustrated in Figure 3. The overhead condenser is an air fin unit. The investment cost for the system was about **\$1.2** million.

An all new system is also being put in at the Farmland Enid Plant to serve both ammonia plants there. It is designed to strip over 800 GPM (3.03 M³/minute) of process condensate and CO₂ condensate. Its approximate cost is \$1.4 million.

In retrofitting an existing tower to include a rectification section, it may develop that there is insufficient tower volume/height to serve both rectification and stripping needs in one tower. If this is the case, the existing tower can continue to be used as the stripper and an additional rectification tower can be added as illustrated in Figure 5. This flow configuration also includes the recovery of ammonia from low pressure purge gas.

The Farmland LP process condensate stripper system lends itself to the use of readily available low cost low pressure used columns and exchangers in the event equipment is not already on hand. It can also be combined in a manner to concurrently recover ammonia from purge gas, therefore controlling the air emission of ammonia, methanol and nitrogen oxides with one system. Also it is flexible dependent on plant needs and equipment available. LP PCS systems now in operation use both liquid cooled and air fin cooled overhead condensers and both direct steam injection and heat input via reboiler.

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